Ammonia Formation and Utilization in Lean NO_x Trap Catalysts: Experimental Determination of Reaction Pathways

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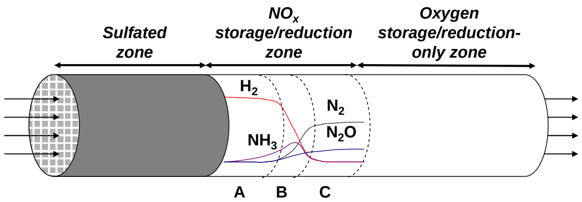
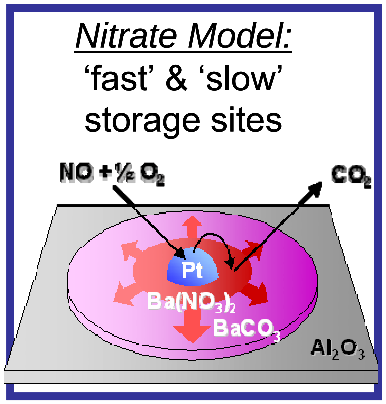
Background & Motivation

Basic Chemistry:

- Conceptual model of S impact on NH_3 slip
  - Need to develop NH_3 SpaciMS capability

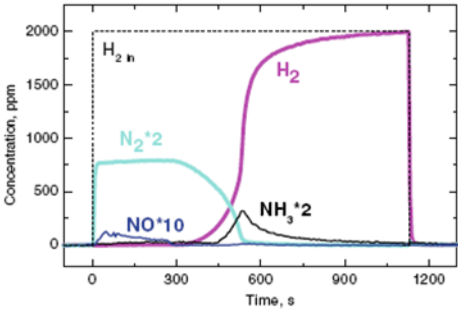


- Nature of NH_3 formation; "fast" vs. "slow" sites?



- Role of NH_3 in regeneration
  - H_2 & NH_3 equivalently effective
  - NH_3 acts as a H carrier?

NH_3 created at 'slow' sites, & follows N_2 and reductant slip



Nova et al. (2007) Topics in Catalysis

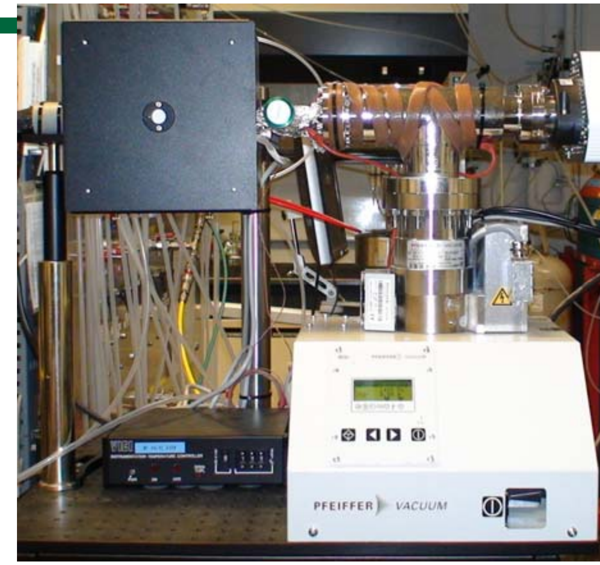
Catalyst Design:

- Minimize NH_3 slip in LNT systems
- Manage NH_3 in hybrid LNT-SCR systems

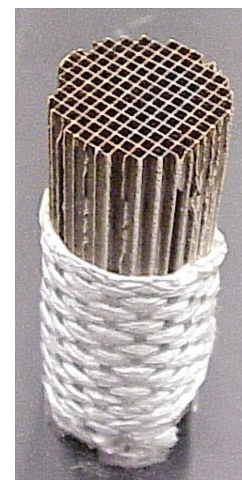
Goals

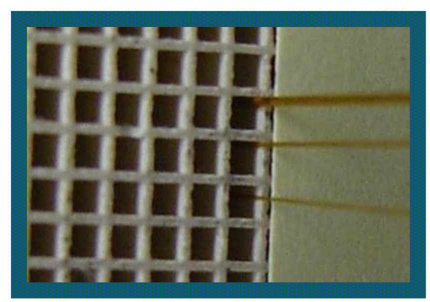
- SpaciMS intra-catalyst transient NH_3 measurements
- Resolve timing of species transients along catalyst
- Investigate temperature effects
- Elucidate regeneration pathways

Approach



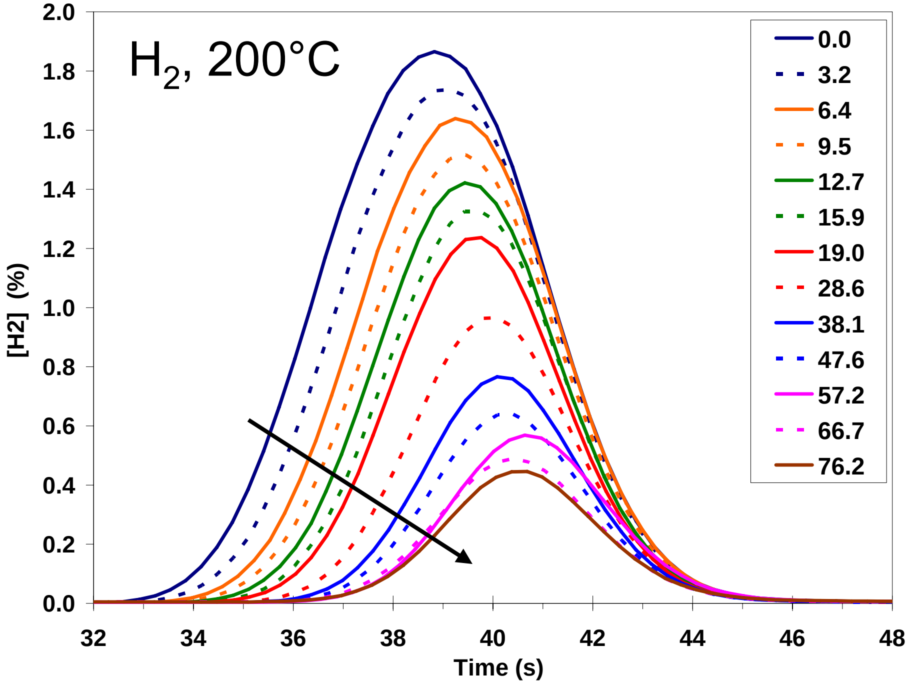
- Catalyst core (3/4” x 3”) on bench reactor
- Washcoat: Pt/Ba/Al_2O_3 model catalyst
  - No cerium – oxygen-storage component
- CLEERS standard short cycling:
  - 60-s lean: 300ppm NO + 10% O_2
  - 5-s rich: 2% H_2
  - Common: 5% H_2O + 5% CO_2 + 100ppm Kr + Ar balance
  - SV: 30k hr^{-1}
- Two mid-catalyst temperatures:
  - 200 & 325°C
- Resolve species distributions along catalyst channel
  - SpaciMS
  - 13 locations along channel
  - NH_3 generation and utilization
  - NO_x, N_2 and H_2

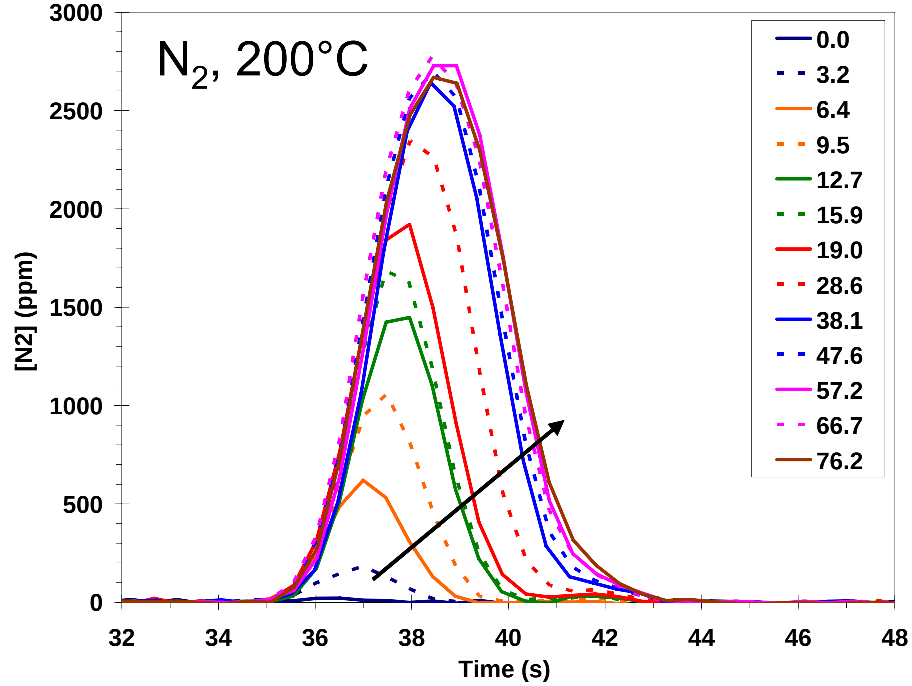




Temporally Resolved Species Distributions

Nature of H_2 & N_2 Transients are Distinctly Different



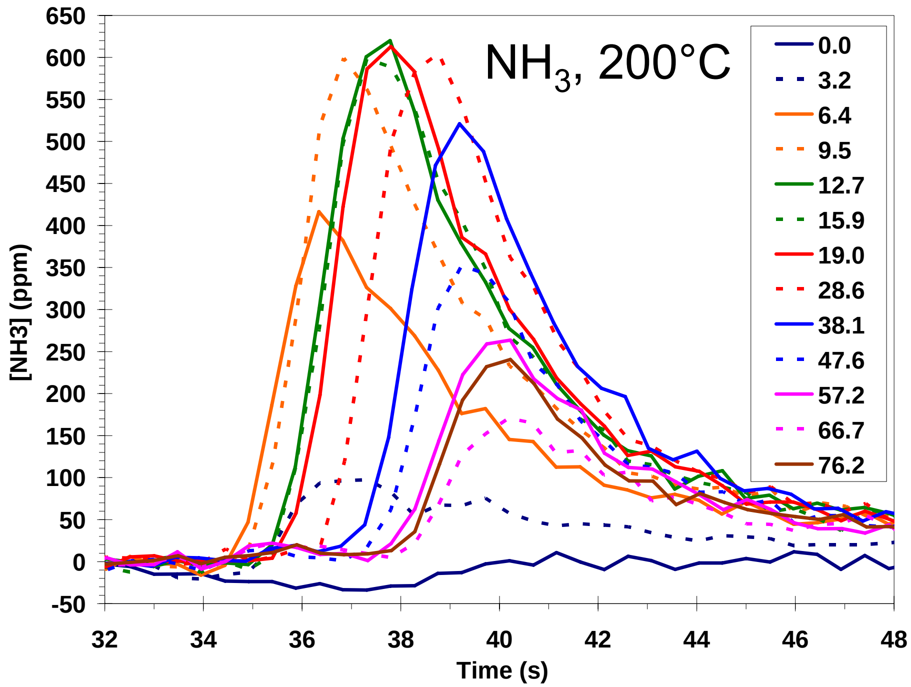


At a given location:

- H_2 consumed at early regen times
- H_2 slips at later regen times

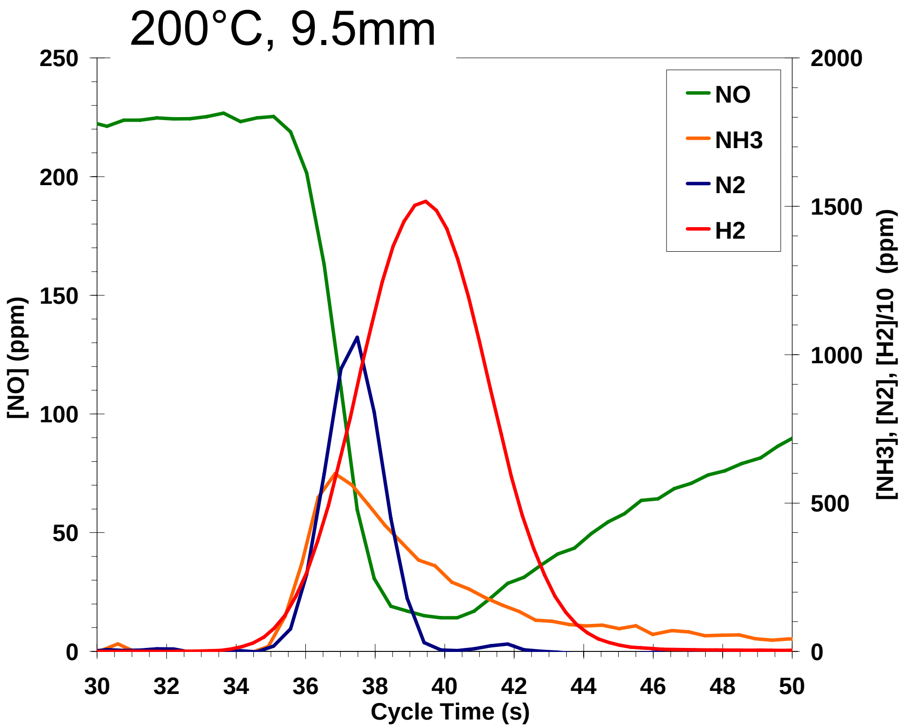
- N_2 slips from upstream locations at early regen times
  - integral effect
- Local N_2 generated at later times
- Little N_2 generated at L>38mm

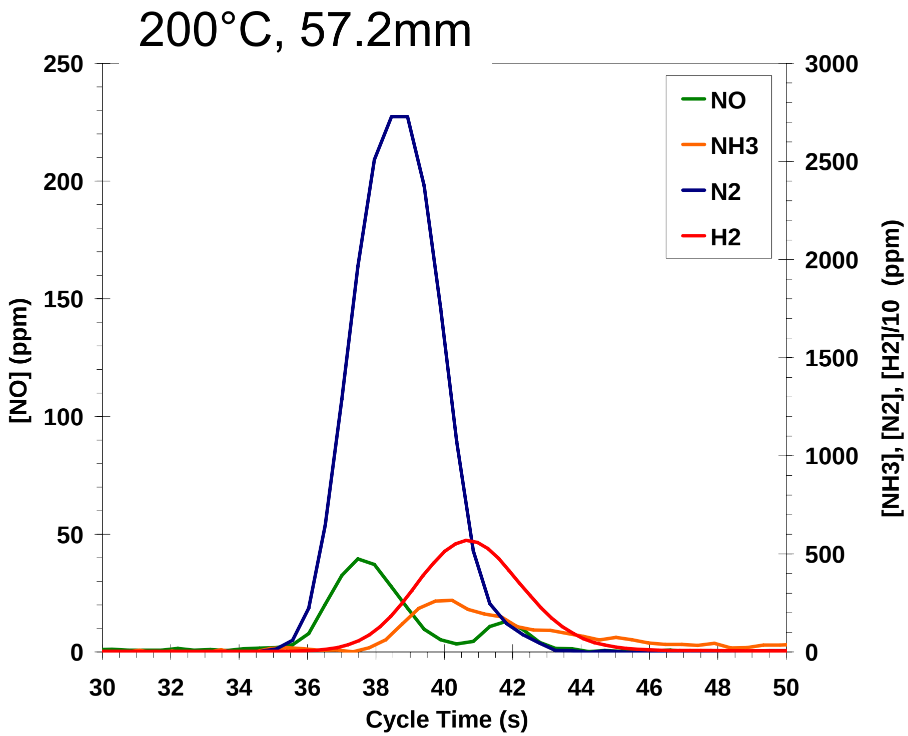
Ammonia Exists at Early Regen Times Inside Catalyst



- NH_3 onset time varies
- NH_3 onset tracks H_2 onset
- Steep leading edge & no early slip
  - aggressive local consumption
- NH_3 may slip at late regen times
- Shows nature of reductant
- Long tail is instrument broadening
- 3 general regions:
  - Buildup: 0-9.5 mm
  - Balanced: 9.5-28.6 mm
  - Deficit: 28.6-76.2 mm

Similar N_2 & NH_3 Generation Timing Inside Catalyst





- At 9.5mm N_2 & NH_3 are generated at similar early regen times
- N_2 & NH_3 profiles more like parallel than consecutive reactions
- At 57.2mm observe typical N_2, H_2, NH_3 catalyst effluent sequence
  - This is an integral effect
- SCR reactions occurring

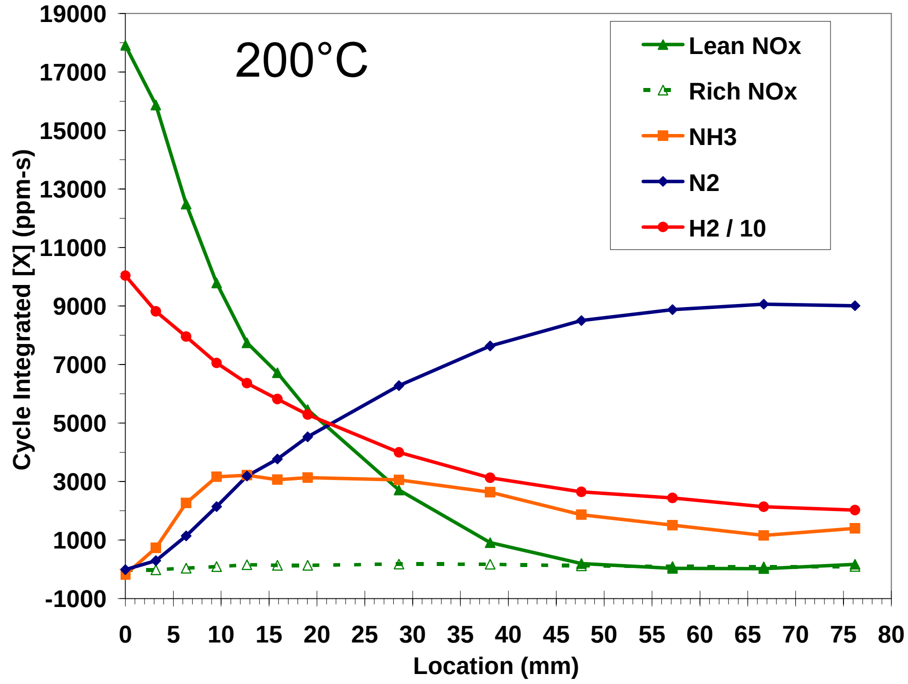
Integral Effects Obscure True Catalyst Nature

What we've learned so far..

- NH_3 generated on same timescales as N_2 at front locations inside the catalyst
- NH_3 is aggressively consumed at its temporal front
- SCR reactions occur
- Simultaneous N_2 & NH_3 suggests parallel N_2 & NH_3 regeneration pathways
- N_2 slips at early regen times from location to location
- Typical N_2, H_2, NH_3 effluent sequence is an integral effect
- Even our 3-mm intra catalyst sections show integral effects
- Integral effects obscure true catalyst nature

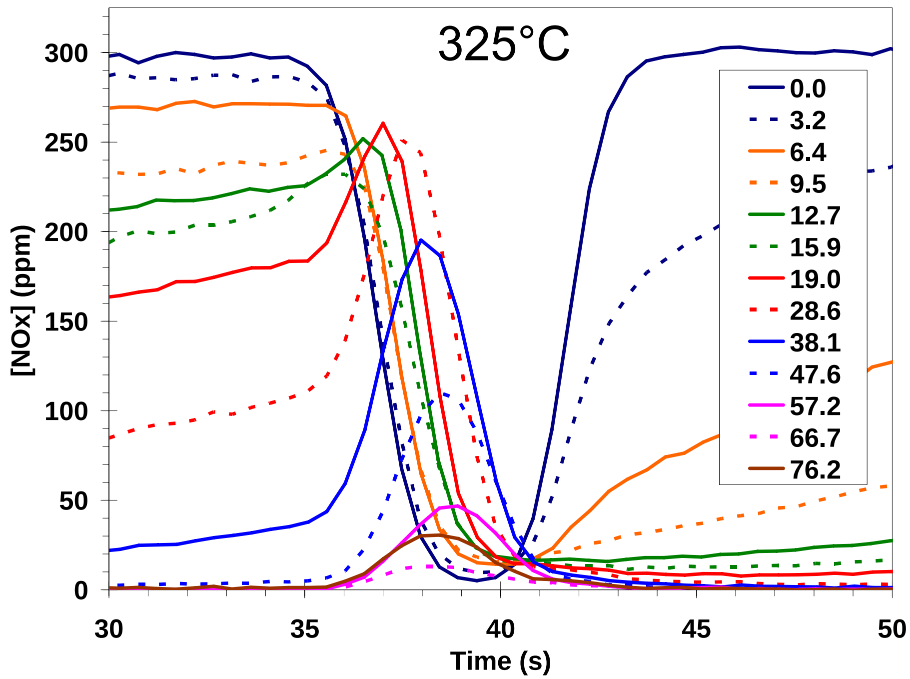
Cycle-Integrated Species Distributions

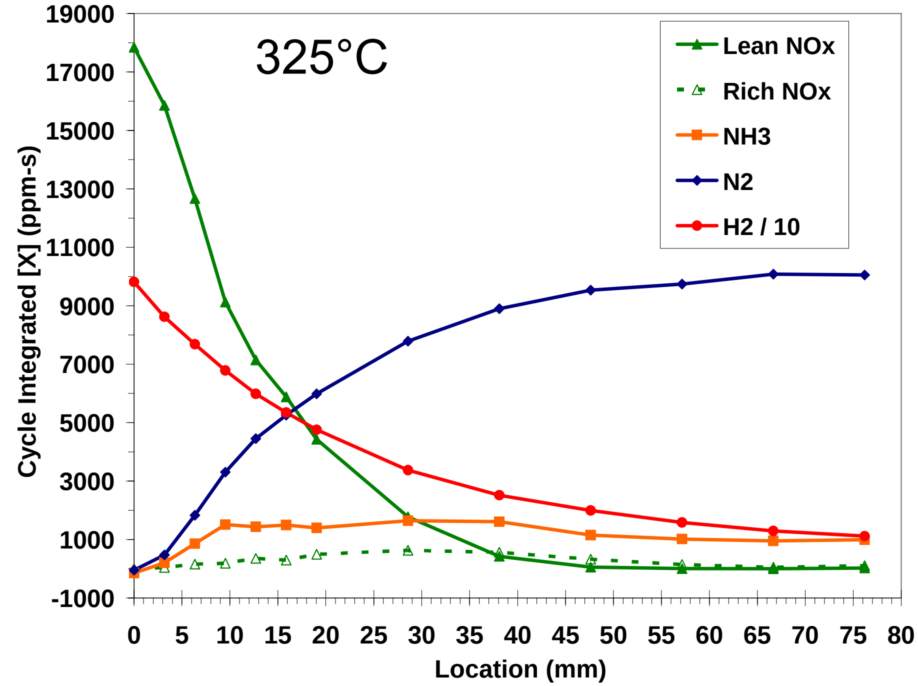
200°C Cycle Integrated Distributions



- NSR zone 0-47.6mm
- 50% NO_x stored in ca. 0-10mm
- Negligible rich-phase NO_x puff
- 3 distinct NH_3 regions
- NH_3 buildup in high NO_x density zone
- NH_3 consumption beyond NSR zone

325°C Cycle Integrated Distributions

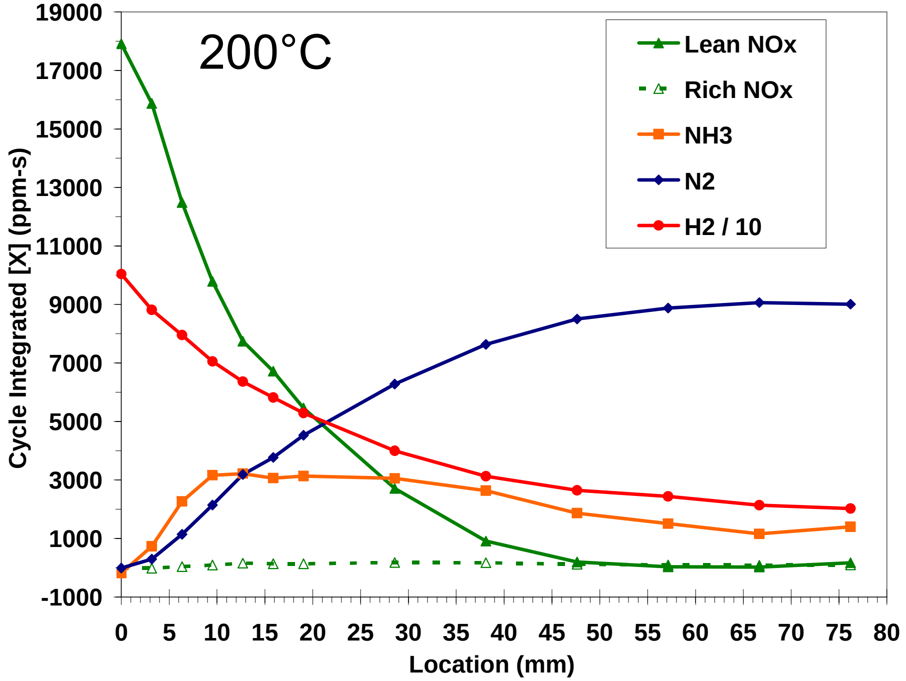


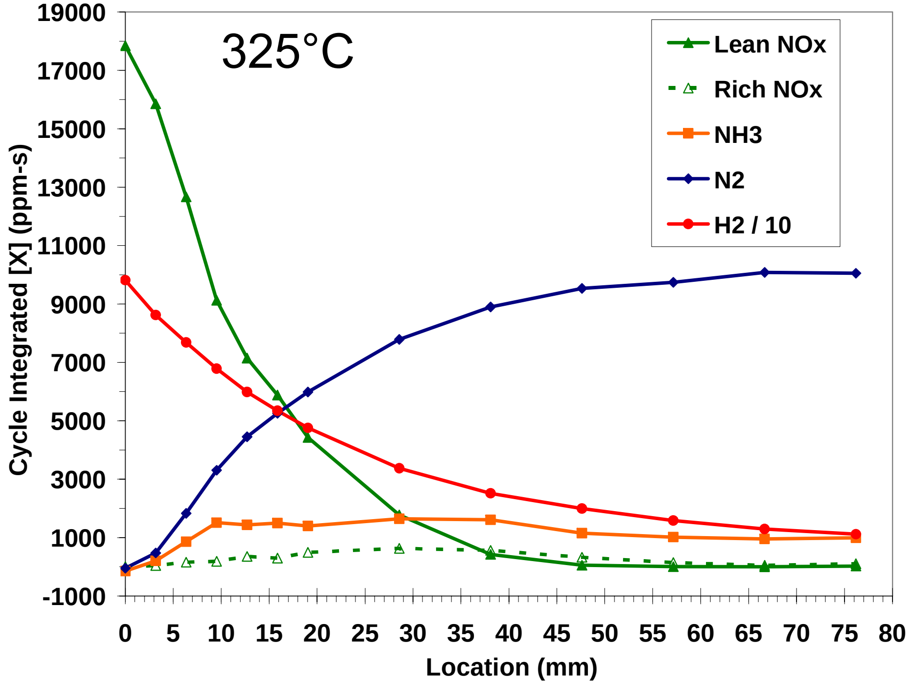


- Significant rich-phase NO_x puff
- Less stable & more mobile NO_x
  - Lower H_2/NO_x ratio
- Lower NH_3
  - Consistent w/ lower H_2/NO_x

- Same 3 distinct NH_3 regions
- Transient NH_3 timing similar to 200°C
  - NH_3 at early regen times
  - Aggressive NH_3 consumption at front

NO_x Distributions Similar but NH_3 Differ at 200 & 325°C





- Similar Lean NO_x distributions
  - Equivalent regen effectiveness
- Similar H_2 Distribution
- Different NH_3 Distribution
- Implies parallel N_2 and NH_3 regeneration pathways

- Amount of NH_3-pathway regen varies at 200 & 325°C
- Pathway partitioning varies with Temp.
  - Consistent with H_2/NO_x NH_3 dependence
- Equivalent regen effectiveness of H_2 and NH_3 (consistent with literature)

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H_2 Regeneration Occurs Via Parallel Pathways

$$Ba(NO_3)_2 + H_2 \xrightarrow{k_{N2}} N_2 + BaO + H_2O$$

$$Ba(NO_3)_2 + H_2 \xrightarrow{k_{NH3}} NH_3 + BaO + H_2O$$

$$NH_3 + Ba(NO_3)_2 \xrightarrow{k_{SCR}} N_2 + BaO + H_2O$$

- Pathway selectivity (k_{N2} / k_{NH3}) varies with H_2/NO_x
  - > Temp : > NO_x puff : < H_2/NO_x : < NH_3 : favors Direct H_2 pathway
  - Variation in k_{SCR} can affect apparent [NH_3]
- Regeneration effectiveness doesn't vary with pathway partitioning
- Global stoichiometry doesn't vary with partitioning
  - Via Direct H_2:
    - $Ba(NO_3)_2 + 5H_2 \rightarrow N_2 + BaO + 5H_2O$
  - Via Intermediate NH_3:
    - $Ba(NO_3)_2 + 8H_2 \rightarrow 2NH_3 + BaO + 5H_2O$
    - $3Ba(NO_3)_2 + 10NH_3 \rightarrow 8N_2 + 3BaO + 15H_2O$

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Summary & Conclusions

- NH_3 is generated synchronous with N_2 inside the catalyst
- NH_3 from "Slow" NO_x sites not observed in our fast cycling experiments
- Integral effects obscure actual intra-catalyst chemistry
- H_2 regeneration of LNTs apparently occurs through parallel Direct H_2 & Intermediate NH_3 pathways
- Partitioning between H_2 & NH_3 pathways appears to vary with temperature
  - Favors NH_3 pathway at lower temperatures
- Partitioning apparently driven by local H_2/NO_x stoichiometry
- Regen effectiveness independent of partitioning btwn. N_2 and NH_3 pathways
- k_{SCR} can vary w/ $[NO_x]_{Local}$ & T and affect apparent k_{N2} & k_{NH3}
- NH_3 oxidation occurs beyond NSR region (supports S effects work)

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Thank You

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